

IN SITU X-RAY ABSORPTION SPECTROSCOPY OF ELECTRODE SURFACES IN TRANSMISSION AND REFLECTION

Hans -Henning Strehblow
Heinrich-Heine-Universitaet-Duesseldorf
Universitaetsstr. 1, Geb. 2642,
D-40225 Duesseldorf, Germany

X-Ray Absorption Spectroscopy (XAS) is an excellent method for in situ studies of the chemical composition and structure of electrode surfaces. The absorption by a water layer may be overcome by the high intensity of synchrotron radiation and a sufficiently high energy of the absorption edge of the element under study. The position and shape of the leading edge of an absorption spectrum gives information on the chemical state of the elements at the surface in addition to ex situ XPS studies whereas the Extended X-ray Absorption Fine Structure (EXAFS) provides the near range order even for non crystalline layers or partial monolayers. The most difficult situation for experiments and data evaluation is EXAFS of thin layers on surfaces of the same metal, like anodic oxide layers on a metal substrate, although this is very interesting for most corrosion problems. In this case EXAFS with grazing incidence below the critical angle of total reflection (RefLEXAFS) suppresses the contribution of the substrate to a large extent, however, not completely. The evaluation of the RefLEXAFS data requires the comparison and a close fit with simulated data starting with results on standards in transmission mode or calculations with programs like FEFF and the calculation of the complete refraction index $n(E)$ with a Kramers-Kronig-Transform (Fig.1) [1]. Even a multilayer sequence for the anodic film may be evaluated by applying the Fresnel equations. The data evaluation yields the related parameters for the near range order i.e. the radius R_j and the coordination number N_j and the mean square displacement σ_j^2 of the related coordination shell j .

Examples are given for the investigation of anodic films on Cu/Ni alloys with an inner Cu_2O - and an outer NiO-part. Furthermore anodic films on silver in 1 M NaOH are studied with thin disordered Ag_2O films at $E = 0.40$ V at the beginning of oxide formation and thicker better ordered films at higher potentials. Thick AgO-layers form at $E \geq 0.725$ V with up to 8 visible coordination shells in the Fourier transform. The detailed evaluation of the first two overlapping coordination shells support the interpretation of the oxide as $\text{Ag}(+)\text{Ag}(3+)\text{O}_2$ with a characteristic increase of the coordination number for Ag^{3+} from 2 to 4 with increasing potential (Fig. 2). This oxide is seriously oxygen deficient according to XPS investigations approaching a ratio $N_{\text{O}}/N_{\text{Ag}} = 0.75$ for $E = 1.1$ V only in comparison to the value 1 for a stoichiometric compound [2].

The study of layers on a foreign metal substrate is much easier if the absorption edges of the involved elements are far apart from each other. Cu-UPD layers on Pt-clusters on graphite and their oxidation and reduction in 0.1 M NaOH are one example [3]. These electrodes may be studied by EXAFS in transmission due to their large surface area. The complete oxidation and reduction of a monolayer (without Cu loss) prevents the contribution of a residual Cu-substrate. The coordination shells contain however also contributions of the Pt substrate.

Cu-UPD from 0.0005 M CuSO_4 in 0.5 M H_2SO_4 on high index planes of Pt (533) single crystals yield interesting details on their amount and site in dependence on the electrode potential [4]. At positive potentials a decoration of the steps of the terrace is obtained with a coordination number 2 for the first two coordination shells (Cu-Pt, Cu-Cu) corresponding to their location at the upper edge position. The lower edge position is occupied by coadsorbed sulfate. With decreasing potential the terrace positions are occupied with a related increase of the coordination number of the Cu-Atoms.

References:

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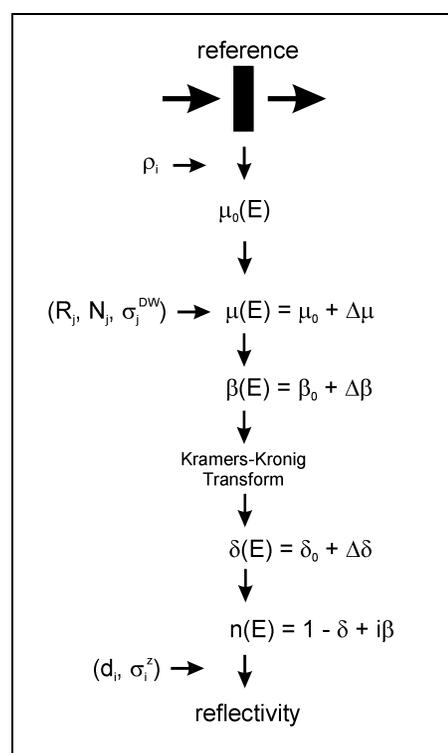


Fig.1: Scheme for calculation of RefLEXAFS and the determination of the short range order.

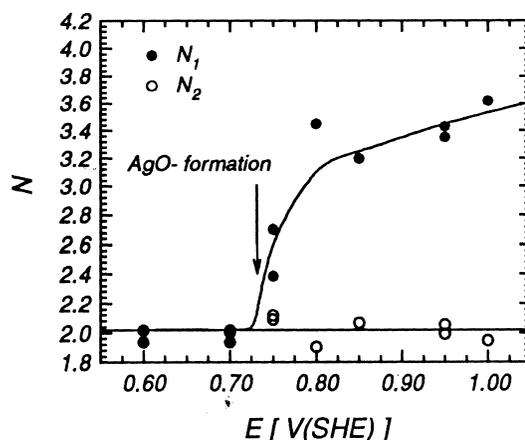


Fig. 2: Coordination number of the 2 first coordination shells of Ag in anodic AgO from RefLEXAFS data.